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The Production of Lustres

THE PRODUCTION OF LUSTRES BY THE USE OF BISMUTH AND COPPER

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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THE PRODUCTION OF LUSTRES USING SALTS OF COPPER AND BISMUTH.

Part 1.

INTRODUCTION.

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The production of metallic lustres as a means of decorating pottery has a very interesting history. The first appearance of this mode of ornamentation was, as nearly as can be established, observed in ware produced in Cairo, probably by Arabian potters, in 1040 A.D.[1] Lustred ware was produced in Majorca as early as 1115 A.D.[2] This pottery was of Moorish workmanship, the decorations consisting of Arabesques traced in a golden lustre.

Contemporaneously, and even perhaps antedating this time, lustred ware was produced in Persia and Spain. The Persian ware was for the most part colorless and opalescent and very little data or description concerning it has come down to the present day. On the other hand, the Spanish lustre work, which was undoubtedly inherited from the Moors, was of the tinted, solid color type.[3] The art survived in Spain as late as 1785 A.D. and in consequence there is available a quantity of fairly accurate data concerning it. As before stated, Spanish lustre consisted for the most part of golden tints obtained by the use of copper, iron oxide, sulphur, and sometimes a little silver. The lustre was applied, to ware bearing a lead-tin glaze. Although each locality had its own peculiar manner in the way in which the lustre was to be produced, the methods used throughout the country were essentially the same.

In England, copper lustred ware was produced during the 18th century.

[1] Furnival - Leadless Decorative Tiles, Faiences and Mosaic - Page 740
[2] M.L.Solon - Italian Majolica - Page 20.
[3] Furnival - Leadless Decorative Tiles, Faiences and Mosaic - Page 740.

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The manufacture is said to have become extinct before the beginning of the 19th century and did not reappear until the rediscoveries of DeMorgan (English) and Parocci and Carocci (Italian). In his work, DeMorgan produced copper and silver lustres by mixing the oxides of the metals with kaolin and gum arabic, and applying this to glazed ware. The heating was carried to low red color (550°C approximately), after which strong reduction was obtained, usually by means of throwing green wood into the kiln chamber. Solon,[4] in his book on Italian Majolica, also speaks of the importance of this reduction.

Another method of pottery decoration, which is often confused with true lustering, consists of causing a thin metallic film of some metal not readily oxidized, to be deposited on the ware by driving off the vehicle used to carry the metal.[5] Thus a bright gold deposit may be obtained by firing a gold sulfide balsam of sulphur solution. This method cannot be considered to produce true lustres.

[4] M.L.Solon - Italian Majolica - Page 15.
[5] Hainbach - Pottery Decorating - Page 192.

PART 2.

PURPOSE OF THE INVESTIGATION.

An investigation of this sort should cover the following points:-

1. What sort of a glaze is best fitted for this method of decoration?
2. Does each particular lustre require its own peculiar glaze?
3. What limits, if any, should there be in the hardness (fusibility) of the glaze?
4. Is tin necessary for the production of lustres and what are the limits to be observed in its use?
5. What temperatures are suitable for producing lustres?
6. With the lustres of copper and bismuth in mind, what is the best and most economical recipe?
7. How and to what extent should the reduction be obtained?

Much of the work done was rather in the way of establishing the relation between fact and legend as encountered in the literature on the subject. In most cases, such data obtained, was given in extremely empirical form, and in many cases, the materials named in recipes were given in old chemical nomenclature, which was quite unrecognizable. In several cases, materials could not be obtained. A notable example of this was encountered in a recipe for bismuth lustre. In this case, oil of spike was prescribed, but on investigation it was found that any essential oil was satisfactory.

Owing to the shortness of time and to the writers inability to produce a true bismuth lustre, none of the points above enumerated were determined for bismuth, although all points were covered in the investigation of copper lustres.

PART 3.

GLAZES USED IN THIS INVESTIGATION.

In order to determine the glaze best suited for receiving lustre, a series of four glazes of the whiteware type were prepared. These glazes were all leadless-boric acid glazes and were largely fritted. The glazes were numbered 1, 2, 3 and 4, the ceramic formulae being as follows:

1. $\left.\begin{matrix}0.23\ K_2O \\ 0.33\ Na_2O \\ 0.44\ CaO\end{matrix}\right\}$ $\left.\begin{matrix}0.754\ Al_2O_3 \\ 0.66\ B_2O_3\end{matrix}\right\}$ 2.03 SiO_2

2. $\left.\begin{matrix}0.32\ K_2O \\ 0.34\ Na_2O \\ 0.15\ BaO \\ 0.19\ CaO\end{matrix}\right\}$ $\left.\begin{matrix}0.21\ Al_2O_3 \\ 0.39\ B_2O_3\end{matrix}\right\}$ 3.95 SiO_2

3. $\left.\begin{matrix}0.105\ K_2O \\ 0.307\ Na_2O \\ 0.588\ CaO\end{matrix}\right\}$ $\left.\begin{matrix}0.589\ Al_2O_3 \\ 0.615\ B_2O_3\end{matrix}\right\}$ 2.67 SiO_2

4. $\left.\begin{matrix}0.4\ KNaO \\ 0.1\ BaO \\ 0.1\ MgO \\ 0.2\ ZnO \\ 0.2\ CaO\end{matrix}\right\}$ $\left.\begin{matrix}0.32\ Al_2O_3 \\ 0.3\ B_2O_3\end{matrix}\right\}$ 3.0 SiO_2

The maturing temperatures of the several glazes were as follows:

Glaze 1 - Cone 3.
Glaze 2 - Cone 3.
Glaze 3 - Cone 4.
Glaze 4 - Cone 1.

The glazes were prepared by fritting all the materials but the clay, this being excluded so that it might have the effect of floating the hard settling frit. Fritting served also to mix the glaze constituents more intimately than otherwise would have been possible. After the frit was dried and weighed, one half of each batch was compounded with .25 equivalents stannic oxide. Thus

when prepared, each glaze batch consisted of two end mixtures, one of which contained no tin and the other having .25 equivalents tin. The ends were then blended, on the basis of the dry weight of the glaze, to give different series for each glaze: as

No. of Series	0	1	2	3	4	5
SnO_2 Content	.00	.05	.10	.15	.20	.25

This made a field of 24 glazes to be investigated. The glazes were applied to bisque tiles by dipping and were burned to their respective cones in wadded saggars.

RESULTS OF GLOST BURN AND APPEARANCE OF GLAZES.

Group 1 - Slight immaturity was observed, even at Cone 4. This was probably due to poor heat distribution in the kiln. All series of this glaze showed marked crazing. The opacity or whiteness was poor even at .25 SnO_2. In general, the glaze was found unsuitable for the application of lustres.

Group 2 - These glazes have a fine even texture and showed small tendency to craze. This crazing decreased with additions of tin. All glazes containing any tin showed fine white opacity.

Group 3 - The appearance of the different series of this group was very similar to that of Group 2, except that in the different series, the effect of the increase of tin showed very plainly, the higher the tin content, the whiter the glaze.

Group 4 - This glaze gave a very good clear surface, but appeared to have a tendency to crack in the early stages of firing. These cracks, most of which healed after the glaze became fluid, showed more or less in the finished piece. The glaze itself gave a very brilliant surface and produced a very beautiful white enamel with all proportions of tin.

PART 4.

DISCUSSION OF THE CAUSES OF THE FORMATION OF LUSTRES.

The mechanism of the lustring process is rather obscure, but seems to consist in the deposition of some reduced form of the salt of the metal used. Guy Maw, F. S. A.[1] writes, " A thin film of metal in the liquid form is applied to a pottery body, usually mixed with balsam of sulphur and oil of turpentine. When fired, the reduced metal in a state of extreme tenuity shows its characteristic lustre without burnishing. To the gold, silver, copper, and bronze lustres may be added pink, which is obtained from a precipitate of stannic chloride and gold chloride, known as Purple of Cassius." Whether the lustre is produced by the reduction of the metal or the deposition and subsequent embedding, of a lower oxide of the metal is not absolutely known. As evidence in favor of the metallic film theory, the writer is able to state that he has obtained globules of metallic bismuth by simple reduction without the use of a flux. From this, it does not seem to much to assume that at least part of the oxide is reduced to metal in producing lustres, of this type. The temperature necessary for this metallization is about 550°C, that is, low red heat.

PART 5.

METHOD OF PREPARING COPPER LUSTRES.

The methods used in applying the lustre coat to the ware are, generally, three:

1. By mixing the salt with some inert material which can be removed by scraping after the reduction has been accomplished.

2. By preparing the lustre by adding the salt of the metal, in aqueous solution, to a resin soap or sodium resinate, to give a precipitate of metallic salt in sodium resinate. This method is, of course, only possible in the case of a salt soluble in water.

[1]House Beautiful - Vol XLVII - Page 284.

The method described by Hainbach[1] for the preparation of the resin soap is as follows:- To a boiling aqueous solution of sodium carbonate is added powdered resin till carbon dioxide ceases to be given off. This indicates that no free carbonate is left. The supernatant clear solution (pale yellow or light brown in color) is decanted off, leaving any undissolved matter and the metallic salt is added to this liquor until a precipitate ceases to form. This precipitate is washed repeatedly in hot water, and dried, and may then be stored and used as needed. In preparing lustres of this sort it is necessary to observed one caution in storing the precipitate: that is, it should be stored in opaque vessels because of the property of metallic resinates losing their solubility in ethereal oils on prolonged exposure to light. As the lustre is to be used, portions of the powdered lustre base are mixed with some ethereal oil to permit of adhesion to the ware during firing.

3. The third method consists in adding metallic salt to melted resin directly, and dissolving the resultant mixture in some ethereal oil. Such oils are oil of lavendar, oil of rosemary, oil of spike-nard and oil of cedar.

PART 6.

METHOD OF INVESTIGATION

Copper lustres - The first investigation conducted was for the purpose of determining the reduction period and the temperature best suited for the production of the typical copper lustre. In carrying out this determination, the simplest lustre preparation was used. It was as follows: To 500 grams of Florida Kaolin was added 50 grams of black copper oxide (CuO) and the whole mixed with 300 c.c. of water in a porcelain ball mill. The mill was run for a half an hour, no attempt being made to grind the mixture. On removal, the slip which was very viscous, was then lawned thru a 40 mesh sieve to insure that no large particles would be present. The lustre, without the use of an agglutinate, was applied to the prepared glazed trial pieces. The firing was done in a

[1]Hainbach - Pottery Decorating - Page 208.

small gas fired, test kiln. The temperature was raised uniformly (approximately 200°C per hour) to 500°C with oxidizing conditions prevailing, and from 500° upward with strong reduction. Trials were drawn from 535°C (the first showing of color in the kiln) every five minutes until all the test pieces had been drawn. The last trials were drawn at a temperature of 600°. This burn included only glazes of Group 1.

TABLE 1.

	Temperatures.				
Series no.	535°	550°	570°	585°	600°
0	No lustre	No lustre	No lustre	No lustre	
1.	"	"	"	Faint lustre	
2.	Dull	Faint Brown	Reddish	Red Color	
3.	No lustre	No lustre	"	"	
4.	Red tinge	Red tinge	No lustre	Good lustre.	
5.	No lustre	No lustre	No lustre	"	

RESULTS.

The results from this burn showed very little, besides defects in the regulation of the temperature and the placing of the trials. The indications, however, were that a lustre was not obtainable (or difficultly so) in the absence of tin. This directly corroborates data already known[1]. It also served to show that past a certain point, increase of temperature and length of reduction period produced little or no effect. In general, the results of this burn showed unsatisfactory trials because the glaze surfaces were poor, the glaze having crazed and pinholed considerably. In certain trials the lustre bearing coat had separated into large cracks, giving a mottled appearance to the lustre.

Before beginning to fire Group 2 trials, an attempt was made to regulate the firing conditions so as to give a more uniform heat distribution. To accomplish this, two base metal thermo-couples were calibrated against a rare metal

[1]Furnival - Leadless Decorative Tiles, Faience, and Mosiac - Page 740.

thermo-couple. These three couples were placed in different positions in the kiln chamber. The trials of Group 2, prepared as in the case of Group 1, were placed and the kiln started. As the temperature was raised the variations in different parts of the kiln were noted and the burners regulated to give a uniform temperature throughout. Trials were drawn as before and the same conditions as prevalent in the previous burn.

TABLE 2.

Series No.	Temperatures 535°	550°	570°	585°	600°
0	No lustre	No lustre	No lustre	No lustre	Brownish Discoloration
1.	Dull	Faint lustre	Good lustre	Good lustre	Good lustre
2.	Faint color	" "	" "	" "	" "
3.	Faint Red	Good lustre	" "	" "	" "
4.	Discolored	" "	" "	" "	" "
5.	"	" "	" "	" "	No lustre deep red color

RESULTS.

This burn seems to show that as long as tin is present, its quantity is of small importance. This fact was also noted by DeMorgan in his work on lustres about 1892. Series 2 and 3 appear to give the best tinting; however, this was probably due to a better glaze surface. This burn establishes the best furnace conditions as 570°C and twenty to thirty minutes reduction period.

It was not thought needful to make such a detailed investigation of the necessary burning treatment for Groups 3 and 4. Trials of each series of both groups were, however, tried using the furnace conditions as determined.

TABLE 3.

Series Number	Temperature 570°C
0.	Discolored
1.	Good lustre
2.	" "
3.	" "
4.	" "
5.	" "

TABLE 4.

Series Number	Temperature 570°C
0.	No lustre
1.	Good lustre
2.	" "
3.	" "
4.	" "
5.	" "

RESULTS.

The discoloration in the case of Group 1 - Series 0 developed in polishing with flint to give a dull surface to the glaze. This may have been an incipient lustre. The burn as a whole showed that the nature of the glaze seems to be of little consequence. All of the glazes tried were moderate temperature glazes, the maturing points of which have been already noted.

The copper lustres produced with the mixing of copper oxide and kaolin, though uniformly successful in producing the desired color effects, were not satisfactory for several reasons. Due to the shrinkage of the raw clay, cracks opened in the lustre-bearing material, causing light lines to appear on the face of the trial where the glaze had been uncovered. The clay and oxide which had

been reduced, formed a hard dense crust which was removed only with difficulty, considerable scouring with powdered flint being usually necessary. As prolonged scouring destroyed the pleasing metallic sheen, it was desirable to replace the raw clay by something that was easily removable. The powdered flint wasavailable and was used as a substitute.

To 500 grams of flint, was added 50 grams of CuO and the two mixed, dry, in a porcelain ball mill for two hours. Part of this, 50 grams, was then taken, mixed with enough water to make a paste and was applied without the use of agglutinants to glazed trial pieces. It was decided at this time to compare the effect of added amounts of copper oxide in the appearance of the luster. In this burn only Series 2 - Glaze 2 was used. The different strengths of copper bearing flint were made up in the following way: After 50 grams of copper oxide and flint had been taken from the ball mill, 50 grams more of copper oxide were added and similarly mixed. Again, a part was taken and 50 grams more of the copper oxide were added and mixed. In this way, four mixes were obtained, having progressively increasing amounts of copper. This method of preparation, while not giving regular increments of copper was judged to be sufficient to show the effect of additions on lustre production.

The trials were burned at 570°C with strong reduction above 500°. The results of this burn were not such as could be readily put in tabulated form. The use of flint was very satisfactory, the crust, in many cases, being removable by merely striking the piece on one of its edges. In no case, was more than a slight polishing necessary to remove all traces of the hard crust. The lustre and color was fully as good and no trouble due to light streaks was experienced. In the event that a vertical or inclined surface was to be lustred, an addition of a gum would probably be necessary. The depth of color varied directly with the proportion of copper oxide used. The trials having the highest amount of copper had all the color "Rouge flambe" glazes, with the addition of a metallic sheen in oblique light. The trial having the smallest amount of copper,

presented a very pleasing pinkish tint. Variations of color existed between the two extremes, though the metallic glint in reflected light was observed in all.

An attempt to produce a copper lustre by preparing the lustering coat by Hainbach's dry method, that is, additions of copper oxide to melted resin with subsequent solution in lavendar oil, brought forth no new effects.

Bismuth Lustre:-

In developing a bismuth lustre, only one glaze - glaze 2- was used. The reason was that the surface of this glaze appeared to be the best of the four glazes tried out, being uniformly free from crazing, pinholing and and other surface defects. This is very important in bismuth lustre work, because much of the opalescence is promoted by the smoothness and brilliance of the glaze. Again the work done on copper lustres seemed to show that any tin containing glaze, of not too high a fusibility, was suitable.

In the first tests made in the development of bismuth lustre the six series of Glaze 2, tin as the variant, were used.[1] In numbering the trial pieces, however, the groupings were according to the method of lustre application. These were as follows:-

Group 1 - Lustre prepared by dissolving the bismuth salt in melted resin, with subsequent solution of the resultant compound in oil of lavendar.

Group 2 - Lustre prepared by the addition of a bismuth salt in aqueous solution to a sodium resinate (resin soap) solution with subsequent solution of the precipitate formed, in oil of lavendar.

Group 3 - Lustre prepared by mixing the bismuth salt with an inert material such as clay or flint in a manner similar to that used in producing copper lustres.

In the preparation of lustre No.1, 50 grams of yellow resin was heated in a porcelain dish until it was completely melted. To this was added 6.7 grams

1. See page 5.
2 Hainbach - Pottery Decoration - page 209.

of $BiO \cdot NO_3$ (bismuth subnitrate) in very small amounts. The addition of the bismuth salt (gentle heating being continued) was accompanied by continual stirring with a small porcelain spatula. As the salt was introduced into the melt a strong evolution of gas of a brownish color was noted. This appeared to be nitrogen dioxide. Such an evolution was rather to be expected as bismuth subnitrate decomposes at 260°C. When all the $BiO \cdot NO_3$ had been added and the melt had become quiet, heating was stopped and the mixture allowed to partially cool, after which 120 grams of oil of lavendar was added, again with stirring. The resultant dark brown viscous liquid was decanted into another container, leaving behind a small mass of dark pitchy material, probably undissolved bismuth resinate.

In the preparation of lustre No.2, a slight discrepancy was unavoidable. Bismuth subnitrate did not dissolve in water, but on heating formed a white flocculant precipitate after an evolution of gas. From the chemistry of bismuth, this appeared to be an oxyhydroxide, as bismuth has a strong tendency to hydrolyze. The precipitate was added to the resin soap solution whereupon another precipitate of a dark brown color appeared. This latter was separated from the mother liquor by decantation, dried and dissolved in lavendar oil, the excess oil being removed by gentle heating till the liquid thickened to the consistency of molasses.

The preparation of lustre No.3 was as has been said, similar to that of the copper lustre.

The burning of the lustres was conducted in accordance with conditions established in the first successful copper lustre burn, i.e. an oxidizing atmosphere up to 500°C, with strong reduction from 500° to the finish.

RESULTS OF BISMUTH LUSTRE BURNS.

GROUP 1.

Temperature	Series.					
	0	1	2	3	4	5
550°C	No lustre	Faint mottled appearance	Mottled white and faint yellow	Faint Mottled	Mottled	Faint Yellow Streak
570°C	"	Mottled	Mottled	Mottled	Mottled	Mottled.

Group 2.

The results of this burn were so similar to those of Group 1, that is was not thought worth while to record them in tabulated form. In general, however, the appearance of the surface of the trials showed an even greater mottled white and yellow appearance. In several trials, streaks of material which were taken to be bismuth oxide (Bi_2O_3) as well as small globules of metallic bismuth, were observed.

Group 3.

This group also did not give any results worth tabulating. Here again, several trials showed metallic bismuth as well yellow oxide. In one trial, two very well defined metallic globules were found partially imbedded in the glaze.

CONCLUSIONS - BISMUTH LUSTRE.

True bismuth lustre as present on specimens of Belleek ware was entirely lacking. In no case was the characteristic iridescence of bismuth lustre developed, though plenty of evidence of the reduction of the bismuth salt to metal or oxide was obtained.

PART 7.

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GENERAL CONCLUSIONS.

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The following conclusions may be drawn from the data obtained in this investigation.

Any glaze containing tin, which is not too infusible is fitted for receiving copper lustres. Glazes maturing at Cone 4 required a slightly longer time to lustre than those maturing at Cone 3. From this it might be predicted that any glaze would take a copper lustre provided its fusibility was taken into consideration.

Tin seems to be necessary for the production of lustres. In the case of the bismuth trials, even the mottled appearance was absent in the absence of tin.

With the glazes tried, 0.1 equivalent of tin gave a very smooth glassy and white surface. Further addition did not accenuate opacity already produced.

Good copper lustres were obtained at 580°C. The depth of color seemed to be as much a function of temperature as the amount of oxide used in the lustring coat.

The metallic bismuth, mentioned before, was obtained at temperatures between 560°C and 580°C. At these temperatures, also appeared the mottled white and light yellow.

The only method of obtaining reduction used was that of cutting off the air supply at the gas burners to cause incomplete combustion. This method proved satisfactory in producing copper lustres.

The amount of copper oxide to be used depends on the depth of color desired. A mixture of 50 grams of CuO and 500 grams of flint produced a good copper lustre, while 100 grams of copper oxide with the same amount of flint, gave a deep "rouge flambe."

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